

CHEMICAL REMOBILIZATION OF CONTAMINANT METALS WITHIN FLOODPLAIN SEDIMENTS IN AN INCISING RIVER SYSTEM: IMPLICATIONS FOR DATING AND CHEMOSTRATIGRAPHY

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ABSTRACT

Metals such as Pb, Zn, Cd and Cu from historical mining activity have been used as stratigraphic markers for dating and provenancing vertically accreted, fine-grained floodplain overbank deposits. This study presents evidence for chemical remobilization of these metals within overbank sediments in the Tyne basin, UK. The evidence includes: breakdown of metal-bearing minerals (sulphides, carbonates, iron and manganese oxyhydroxides); shifts of chemical fractions within zones of relatively low pH towards more soluble and reactive phases; and accumulation of secondary iron and manganese oxyhydroxides at levels related to fluctuating water-table levels or to the breakdown of organic matter. All of this suggests that fine, centimetre-scale, chemostratigraphy using metal concentrations and ratios is unlikely to provide reliable data in river systems that have experienced, or are experiencing, major changes in water-table levels, or pedogenesis. Coarse tens of centimetre- to metre-scale, chemostratigraphy, when applied with caution, may still provide a means of delineating contaminated units. © 1998 John Wiley & Sons, Ltd.

KEY WORDS: chemical remobilization; floodplain; overbank sediments; metals; dating; chemostratigraphy

INTRODUCTION

Metal contamination of sediments in many northern European river basins has occurred as a result of present-day and historic mining and industrial activity (Griffith, 1918; Alloway and Davies, 1971; Davies and Lewin, 1974; Lewin *et al.*, 1983; Bradley and Cox, 1986; Lewin and Macklin, 1987; Leenaers, 1989; Macklin and Dowsett, 1989; Macklin and Klimek, 1992; Merrington and Alloway, 1994; Evans and Davies, 1994; Swennen *et al.*, 1994). Overbank sediments in floodplains act as a focus for deposition and short- to long-term storage of metals (Rang and Schouten, 1989; Marron, 1992; Macklin *et al.*, 1992b; Macklin, 1996) and thus record pollution histories in river basins (Davies and Lewin, 1974; Ottesen *et al.*, 1989; Macklin *et al.*, 1994; Ridgway *et al.*, 1995).

Metal concentrations and ratios have been used as stratigraphic markers for provenancing (e.g. Passmore and Macklin, 1994) and dating vertically accreted fine-grained overbank deposits. The latter has been done in two ways: (1) coarse-scale stratigraphic division, utilizing unit-representative samples to distinguish pre-, peak- and post-mining or -industrial sedimentation (e.g. Davies and Lewin, 1974; Lewin *et al.*, 1977; Macklin and Lewin, 1989; Rang and Schouten, 1989; Macklin *et al.*, 1992a; Sear and Carver, 1996), and (2) fine-scale stratigraphic division, whereby 'contaminated' peak-mining and -industrial units have been further subdivided (e.g. Macklin, 1985, 1986; Klimek and Zawilinska, 1985; Macklin *et al.*, 1992b; Swennen *et al.*, 1994; Taylor and Lewin, 1996).

The underlying assumption for these studies is that the metal concentrations reflect primary depositional signatures. Metals, however, have been shown to be remobilized through biological processes such as uptake in plants and organisms (Koepe, 1977; Adriano, 1986; Alloway, 1990). The phenomenon of chemical remobilization of metals in floodplains has long been recognized (e.g. Lewin *et al.*, 1977; Macklin and Lewin,

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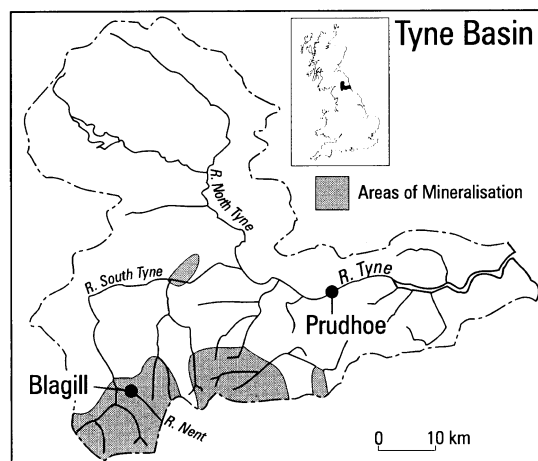


Figure 1. Location of the Tyne basin, NE England, and of the Blagill and Prudhoe alluvial sediment profiles

1989; Rang and Schouten, 1989) but only a few studies (e.g. Bradley and Cox, 1990; Taylor, 1996) have provided documentary evidence for this process. This is surprising, considering that metals have been shown to be slowly leached through temperate soils (Salomons and Förstner, 1984). Fluctuating water-table levels, and acidification through pedogenesis or atmospheric deposition, will cause changes in redox potential and pH. These will in turn alter the forms of contaminant metal.

To explore this further, we have examined: (1) the forms of Pb, Zn, Cd and Cu within two overbank alluvial deposits of the Tyne basin in northern England; (2) the chemical redistribution of metals within sediment profiles; and (3) the validity of metal concentrations and ratios (particularly Pb/Zn) for dating metal-contaminated alluvial sequences. This study is aimed mainly at fine-scale stratigraphic subdivision of contaminated units, although some of the principles outlined are also applicable to coarse-scale stratigraphy. In this paper, 'oxyhydroxide' refers to all oxides, hydroxides and oxyhydroxides, and 'contaminant metals' refers to Pb, Zn, Cd and Cu.

Study basin

The Tyne basin in northeast England drains the northern part of the Northern Pennine Orefield, formerly the most productive lead and zinc mining area in Britain (Dunham, 1990) (Figure 1). Large-scale mining in the South Tyne catchment began in the early seventeenth century following a period of small-scale extraction dating from Roman times (Raistrick and Jennings, 1965). Peak production of Pb took place from 1815 to 1880, and of Zn from 1880 to 1920. On-site processing included gravity sorting in water, froth flotation and smelting. Mining ceased shortly after World War Two.

Seventeenth to nineteenth century methods of mining and mineral dressing resulted in the discharge of large amounts of mine waste into river channels of the Tyne basin. This waste was mainly fine-grained (<2 mm), and consisted of particles of the ore minerals galena (PbS), sphalerite (ZnS) and smithsonite (ZnCO₃), and minor amounts of associated minerals including siderite (FeCO₃), ankerite [(Ca, Mn, Fe)CO₃], and contaminant metal-bearing goethite (FeO·OH) (Dunham, 1990). This waste has been dispersed many tens of kilometres beyond the orefield. Approximately 18 km² of the present-day alluvial valley floor of the Tyne and its tributaries have soil Pb, Zn and Cd concentrations above those considered acceptable by the UK Inter-Departmental Committee on the Redevelopment of Contaminated Land (ICRCL, 1987, 1990).

Vertically accreted historic Tyne alluvium has been dated (Macklin, 1986, 1992; Macklin *et al.*, 1992b) using Pb and Zn concentrations and ratios based on the well documented metal production data for the Tyne basin orefields, especially after 1848 (Dunham, 1944; Raistrick and Jennings, 1965), with different peak production periods of Pb and Zn. Sediments showing high total Pb/Zn ratios were thought to have been deposited prior to 1880, and those showing low Pb/Zn ratios after 1880. This work was based on the assumption that, because of rapid sedimentation rates, the ratios were virtually unaffected by chemical factors such as solution and

adsorption onto fine material, and by a loss of pollutants due to 'chemical exchanges' (Macklin, 1986).

MATERIALS AND METHODS

Two vertical profiles were sampled within overbank sediment deposits. The first, at Blagill (Figures 1, 2), is located in the highly polluted River Nent near the mining areas. The Prudhoe (Figures 1, 3) profile is located in the lower Tyne valley, 60 km downstream of the nearest mine, and is a terrace *c.* 2.5 m above the present river bed. Both sites lie below the level of all but the largest flood. Samples were taken for geochemical and mineralogical analysis from each distinct sedimentary layer. These were air-dried and sieved to <2 mm.

To aid in discussion and presentation, the profiles have been subdivided into zones based on the classification of Gerrard (1992). Riecken and Poetsch (1960) suggested that 'ABC' pedogenetic models for bedrock soils (Soil Survey Staff, 1975) were inappropriate for floodplain overbank sediment soils. Gerrard (1992) recommended that floodplain soils be subdivided into three general horizons based on the degree of waterlogging. These are: (I) a partly oxidized horizon, generally with a high organic matter content; (II) a mottled zone within which water-table levels fluctuate, and thus redox conditions vary; and (III) a suboxic to reduced bluish-green zone which lies beneath the water table.

The dried (but unashed) Blagill and Prudhoe sediments were analysed for total contents of Fe, Mn, Pb, Zn, Cu and Cd by atomic absorption spectrophotometry (Perkin Elmer 5000) and inductively coupled plasma mass spectrometry (ICP-MS, VG Plasma Quad) following an HNO_3 digestion. Analytical precision and accuracy were determined by inserting blind duplicate and reference standard samples, and were generally better than 5 per cent and 10 per cent, respectively. Blanks, inserted at a frequency of 5 per cent were generally below detection limit. Sediment pH was measured in a 1:2.5 air-dried sediment: de-ionized water (DIW) slurry and organic matter content was estimated by loss on ignition at 375°C for 6 h.

Analyses for Fe, Mn, Pb, Zn, Cu and Cd on a phase-specific, operationally defined basis were carried out using a method adapted from Chao (1972) and Tessier *et al.* (1979). This method partitions sediment-associated contaminant metal into the following fractions:

- (1) Exchangeable (Ex): displaces loosely bound cations and anions; 1M MgCl_2 shaken for 1 h, solid:solution ratio 1:10;
- (2) Specifically Adsorbed (Spec): dissolves some carbonates and the most reactive oxyhydroxides; 1M CH_3COONa (pH 5; CH_3COOH), shaken for 5 h, solid:solution ratio 1:10;
- (3) Easily Reducible (Eas): dissolves mainly Mn as well as partly amorphous Fe oxyhydroxides; 0.1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.01M HNO_3), solid:solution ratio 1:20;
- (4) Moderately Reducible (Mod): dissolves mainly amorphous and poorly crystallized Fe oxyhydroxides; 0.4M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (25 per cent v/v CH_3COOH) 99°C, solid:solution ratio 1:20;
- (5) Oxidizable (Ox): decomposes organic matter and sulphides; 30 per cent v/v H_2O_2 , 0.2M HNO_3 , 85°C, solid:solution ratio 1:20; 3.2M NH_4OAc (20 per cent v/v HNO_3) added, shaken for 30 min;
- (6) Residual (Res): dissolves lattice held metals; 25 per cent v/v HNO_3 , heated for several hours to dryness, leached in 10 per cent v/v HNO_3 .

After each extraction step (except the last), samples were centrifuged at 10000 rpm for 15 min. The supernatant was decanted off, filtered, and made up to 50 ml with 0.02M HNO_3 . Between steps, solid residues were washed with DIW and centrifuged for 15 min to remove traces of the previous extractant. This solution was discarded. Duplicates were used to check analytical precision, and the total metal contents of all six fractions were generally within 10 per cent of total metal contents determined by single-stage HNO_3 digestions. Blanks carried through each extraction step were below detection limits. Extractants were analysed by atomic absorption spectrophotometry (Perkin Elmer 5000) with an air/acetylene flame.

Whole-sediment powders were examined by X-ray diffraction (XRD) using a Philips PW1730 instrument with Cu ($\text{K}\alpha$) radiation at 40 kV/20 Ma operating conditions. Fink and Hanawalt search manuals were used to identify mineralogical components.

Polished thin sections of sediment grain mounts were examined using a Jeol JSM 6400 scanning electron microscope (SEM) combined with energy dispersive X-ray spectrometry (EDX) and equipped with a Link

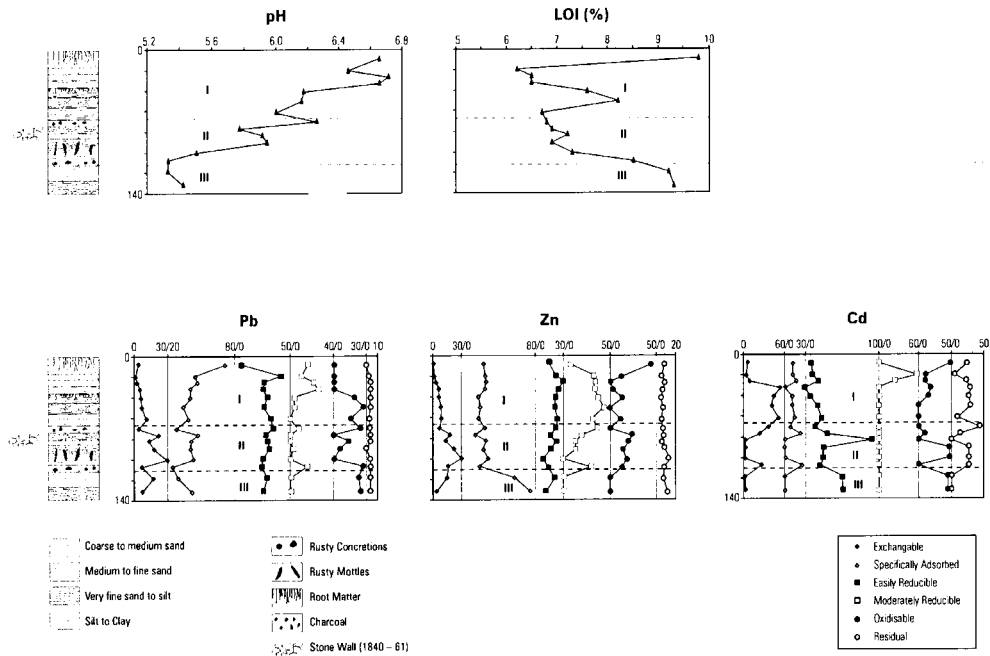


Figure 2. Blagill alluvial sediment profile. Sedimentology, pH, loss on ignition (in per cent), total contaminant metal and Fe and Mn contents (in mg/kg), contaminant metal-bearing mineralogy (in modal per cent), and sequential extraction data versus depth down-profile (in cm). The position and probable age of the stone wall lying 81 cm below the lateral equivalent of the Blagill sediments are also shown. Mn is multiplied by 10 to enhance the contrasts down-profile. Horizontal axes for sequential extraction data represent percentage of total metal for each sequential extraction. Subdivisions for Zones I, II and III are shown

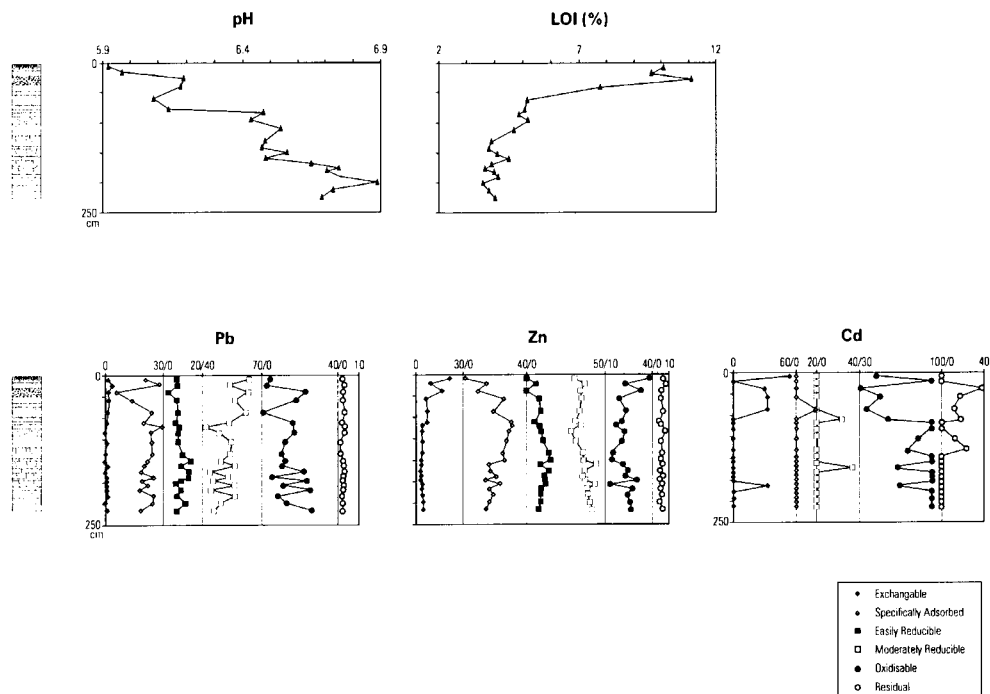
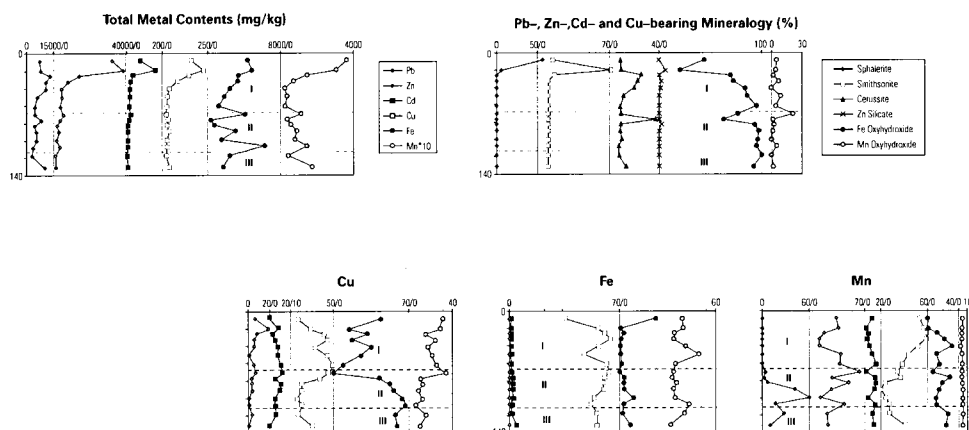


Figure 3. Prudhoe alluvial sediment profile. Sedimentology, pH, loss on ignition (in per cent), total contaminant metal and Fe and Mn contents (in mg/kg), contaminant metal-bearing mineralogy (in modal per cent), and sequential extraction data versus depth down-profile (in cm). Mn is multiplied by 10 to enhance the contrasts down-profile. Horizontal axes for sequential extraction data represent percentage of total metal for each sequential extraction

Blagill



Prudhoe

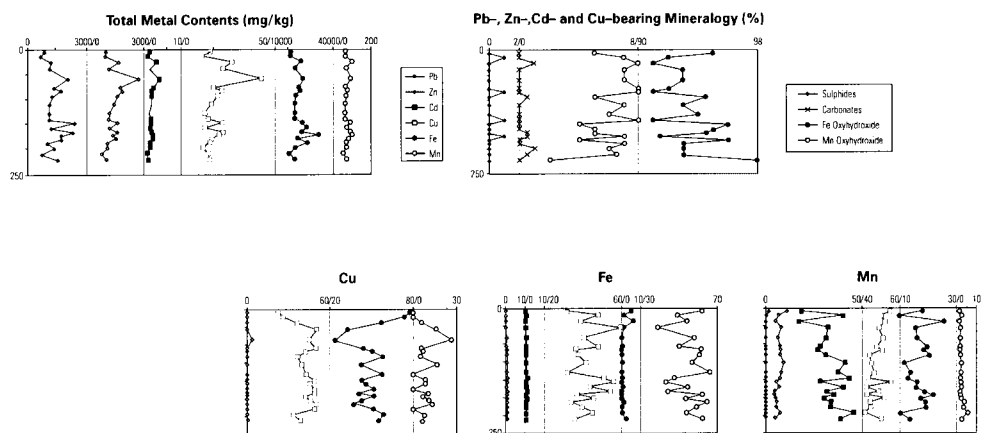


Table I. Summary of Blagill and Prudhoe geochemistry, and of background sediment-borne metal concentrations

	Blagill (<i>n</i> = 15)		Prudhoe (<i>n</i> = 20)		S. Tyne and Tyne late Pleistocene/ early Holocene/ pre-mining alluvium		N. Tyne late Pleistocene/ early Holocene alluvium	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Pb	7070	2770–13 000	1310	615–2340	105*	87–124*	32*	19–56*
Zn	8270	791–38 200	1360	722–2340	85*	73–98*	43*	18–100*
Cd	25.9	1.8–160	3.8	2.6–8.0	0.3†	0.2–0.4†	–	–
Cu	59.2	16.8–228	18.3	11.1–42.5	–	1–10‡	–	–
Fe	33 700	21 700–51 200	22 000	16 800–32 500	–	10 000–60 000§	–	–
Mn	1120	235–3650	765	536–1000	–	100–1000§	–	–
pH	6.02	5.33–6.71	6.45	5.92–6.89	–	–	–	–
LOI	7.6	6.2–9.8	5.4	3.7–11.1	–	–	–	–

n = number of samples; all metal contents are in mg/kg; LOI is loss on ignition in per cent

* *n* = 5 (S. Tyne) and *n* = 11 (N. Tyne) (Passmore and Macklin, 1994)

† *n* = 3, Garrigill pre-mining alluvium (Aspinall *et al.*, 1986)

‡ *n* = 41, Willy Wood Unit (Macklin *et al.*, 1992a)

§ *n* = 82, Shibdon Pond and Blaydon Haughs cores (Passmore *et al.*, 1992)

Analytical backscattered electron detector. Modal abundance of contaminant metal-bearing minerals was estimated using a grain-counting method based upon the work of Davis *et al.* (1993) (cf. Hudson-Edwards *et al.*, 1996).

RESULTS

Blagill

The Blagill profile consists of interbedded fine- to medium-grained sand and silty clay units (Figure 2). It can be subdivided into three zones based on the classification of Gerrard (1992). The upper 67 cm of the profile (Zone I) is partly oxidized, black, and contains root matter. The mixed oxidized/reduced zone (Zone II; 67 to 111 cm) is characterized by rusty mottles and concretions, and varies from black to yellow in colour. The suboxic to reduced zone (Zone III; 111 to 138 cm) is black and lies below the water table.

The lateral equivalents of the sediments above 81 cm lie on top of the stone wall. Historical analysis by Macklin (1986) constrains the age of this wall. An 1820 tithe map suggests that the Nent River channel was stable and of low sinuosity, and showed that enclosure walls had been constructed around the channel perimeter. Further evidence from an 1840 mining map showed that the channel was still stable. However, an 1861 map showed that the enclosure walls had been destroyed with rapid bank erosion and an increase in lateral movement. This suggests that the Blagill sediments lying above 81 cm date from sometime after 1840–1861.

Blagill mineralogy and geochemistry. The results for Blagill pH, loss on ignition, total metal contents, contaminant metal-bearing mineralogy and sequential extractions are shown in Figure 2. Geochemical data are summarized in Table I. The following discussion centres on the relationship between the mineralogical and geochemical data.

Pb-, Zn-, Cd- and Cu-bearing sulphide, carbonate, silicate, phosphate, and Fe and Mn oxyhydroxide minerals occur in the Blagill sediments (Figure 2). Sphalerite and smithsonite are found only in the upper part of Zone I. Sphalerite is pseudomorphed by Fe oxyhydroxides, and by smithsonite, which also occurs as discrete zoned masses (Figure 4a) and as growths on quartz and shale bedrock grains. The sphalerite and smithsonite contain trace amounts of Cd, Cu, Fe and Mn (Bishara, 1966; Vaughan and Ixer, 1980; Hudson-Edwards *et al.*, 1996). Discrete, bladed grains of Zn silicate also occur in the upper part of Zone I. Relatively high Zn, Cd, Cu and Fe contents in the upper part of Zone I (Figure 2) can be explained by these minerals. Oxidizable Zn, Cd, Cu and Fe (Figure 2) are probably caused by the sphalerite, while anomalous levels of both specifically adsorbed and easily reducible Zn, Cd and Cu can be attributed to smithsonite.

Cerussite (PbCO₃) persists throughout the profile. It pseudomorphs galena, and occurs as discrete grains and growths on shale and quartz grains. Occasional Ca-Pb phosphate grains are also present. The specifically

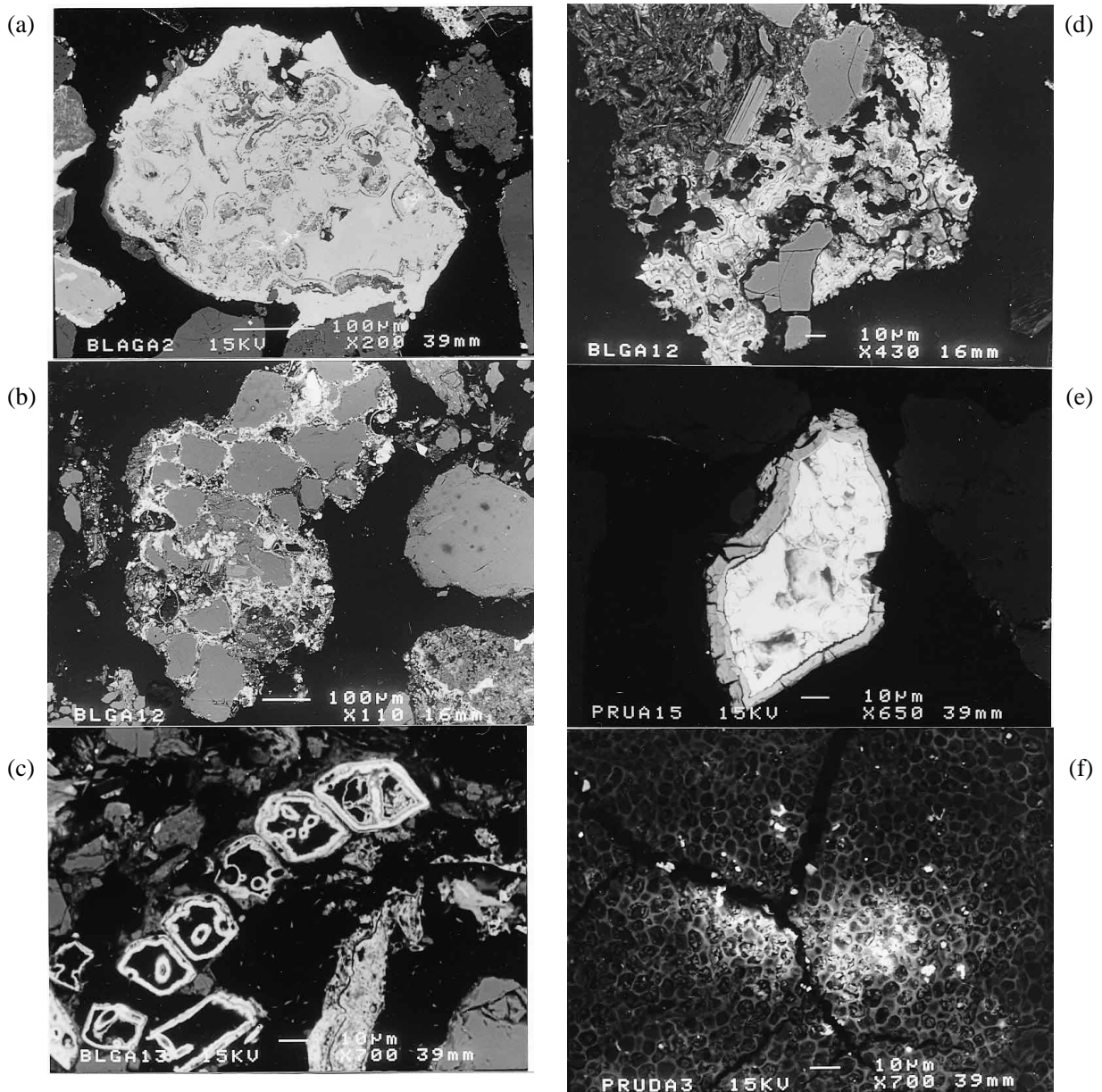


Figure 4. Blagill and Prudhoe scanning electron microscope photomicrographs. (a) Blagill. Zoned and partially massive smithsonite grain. (b) Blagill. Partially disintegrated shale grain, with iron-manganese oxyhydroxides (white) replacing chlorite around quartz (grey) grains. (c) Blagill. Partially disaggregated shale grains, with box-like contaminant metal-bearing iron-manganese oxyhydroxides growing in weathered voids. Note fine-scale zoning of iron-manganese oxyhydroxides. (d) Blagill. Extensive formation of zoned iron-manganese oxyhydroxides (white and grey-white) at edge of shale grain. These textures are interpreted as having formed by accumulation of colloidal oxidation products derived either from underlying horizons by fluctuating water-table levels, or from overlying dissolved constituents. (e) Prudhoe. Chalcopyrite (white) altering to iron-lead-copper oxyhydroxide. Note progressive alteration from rim of grain inwards. (f) Prudhoe. Manganese-lead-zinc oxyhydroxides (white rectangular grains) within cells, and iron-zinc-calcium-phosphate phases (grey) rimming cell walls of charcoal

adsorbed and, possibly, part of the easily reducible Pb fraction can be explained by cerussite (cf. Hudson-Edwards *et al.*, in press).

Fe oxyhydroxides are the dominant contaminant metal-bearing minerals in the lower part of Zone I, and Zones II and III. These pseudomorph cerussite, sphalerite, smithsonite, Zn silicate, siderite, pyrite (FeS_2), and

especially chlorite $[(\text{Mg,Fe,Mn,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8]$. Chlorite-bearing shale grains are progressively degraded down-profile (Figure 4b, c, d). In the lower part of Zone II, zoned Fe-Mn oxyhydroxide precipitates occur in weathered voids within the shale grains (Figure 4c). Fe oxyhydroxides also grow on quartz and occur as discrete, often zoned grains. These occur throughout the profile (Figure 2) but are most abundant in Zone II.

Mn oxyhydroxides also occur throughout the Blagill profile, though to a lesser extent than the Fe oxyhydroxides. They pseudomorph cerussite, chlorite, and grow on quartz and as discrete grains.

Prudhoe

The sedimentology of the sands and silty sands exposed in the river bank at Prudhoe has been described in detail by Macklin *et al.* (1992b). Twenty-five large flood events, which become finer and relatively better sorted up-profile, have been delineated on the basis of sedimentological criteria. The sediments are mainly well bedded and laminated, fine- to medium-grained sands, with some silt and occasional gravel layers. Organic root material is most abundant at the top of the profile (0 to 88 cm), and a layer of charcoal occurs from 23 to 29 cm. A rusty concretionary layer occurs at 173–176 cm. Using Gerrard's classification, the profile has been classified into one zone (Zone I). It lies well (>4 m above low-water level) above the present water table.

Prudhoe mineralogy and geochemistry. The Prudhoe pH, loss on ignition, total metal contents, contaminant metal-bearing mineralogy and sequential extraction results are shown in Figure 3. Contaminant metal contents are generally lower than at Blagill (Table I) but are up to 20 times higher than background values defined for South Tyne and Tyne late Pleistocene, early Holocene and pre-mining alluvium.

Isolated grains of sphalerite, chalcopyrite and cerussite occur in the Prudhoe sediments (Figure 3). These are generally pseudomorphed by Fe and Mn oxyhydroxides (e.g. Figure 4e). The contaminant metal-bearing mineralogy of the Prudhoe sediments is dominated by Fe oxyhydroxides (Figure 3) and which occur mainly as pseudomorphs of chlorite, siderite and ankerite, and as growths on quartz. High accumulations of bulbous, zoned Fe oxyhydroxide growths on quartz occur from 45 to 76 and 173 to 176 cm. These minerals are mainly represented by moderately reducible chemical fractions. The presence of significant amounts of moderately reducible Pb, Zn, Cd and Mn (Figure 3) suggest that these elements are associated with the Fe oxyhydroxides. More crystalline Fe oxyhydroxides may have been extracted as a residual fraction (Figure 3) but this fraction probably also represents other Fe-bearing minerals such as chlorite.

Mn oxyhydroxides form a minor component of the Pb-, Zn-, Cd- and Cu-bearing mineralogy (Figure 3). These occur mainly as growths on quartz and pseudomorphs of chlorite. Very fine (<1 µm) Mn-Pb-Zn oxyhydroxides are also located in the centres of the cells of charcoal (Figure 4f). Some of these cell walls are also lined with Fe-Zn-Ca phosphates. The Mn oxyhydroxides are extracted mainly as easily reducible and, to a lesser extent, specifically adsorbed fractions (Figure 3).

DISCUSSION

Primary deposition and secondary remobilization of metals

The changes in mineralogy and geochemistry which occur down-profile at Blagill and Prudhoe are probably due to a combination of primary (depositional) and secondary (remobilizational) processes. These are considered below.

At Blagill, the sulphides galena and sphalerite are pseudomorphed by the carbonate minerals cerussite and smithsonite. Below 36 cm in Zone I, the smithsonite completely disappears while the cerussite persists (Figure 2). This may be mainly a depositional change, marking the start of intensive Zn mining in 1880. This fits stratigraphically with the assigned date of the underlying stone wall (1840–61). The presence of cerussite above 36 cm would thus be due to ongoing Pb mining after this time. However, this is inconclusive because there is evidence of complete pseudomorphing of sphalerite and smithsonite by Fe and Mn oxyhydroxides below 36 cm, suggesting that they *were* present at the lower levels. Recognizable sphalerite and smithsonite pseudomorphs below 36 cm are relatively uncommon (<5 per cent of all Fe and Mn oxyhydroxides), but may not be totally representative of the original amounts of these minerals present, given that they may have completely weathered and left no trace. In addition, the persistence of cerussite relative to smithsonite below

36 cm may also be due to the lower solubility of cerussite relative to smithsonite at the slightly acid pH of these sediments (Garrels and Christ, 1965; Krauskopf, 1967).

Changes in the Fe- and Mn-oxhydroxide metal associations are also noted within the Blagill and Prudhoe profiles. At Blagill, sequential extraction data suggest that under near-neutral pH conditions in Zone I, the Fe oxyhydroxides are extracted mainly as moderately reducible fractions, and the Mn oxyhydroxides as easily reducible and specifically adsorbed fractions (Figure 2). Moderately reducible Mn may be ascribed to Mn-bearing Fe oxyhydroxides or crystalline Mn oxyhydroxides. These, and the associated contaminant metal affinities, change down-profile in Zones II and III.

The decline in moderately reducible fractions of Pb, Zn, Cd and Mn from Zone I to Zone II may be related to a depositional change in input species over time (cf. Evans and Davies, 1994). However, moderately reducible contaminant metal generally forms a significant portion of total metal in contemporary Tyne overbank sediment (Macklin and Dowsett, 1989; Hudson-Edwards *et al.*, in press), which represents eroded material from deposits of different age. Thus, the Blagill moderately reducible fraction decline may instead be caused by the breakdown of Mn-bearing Fe oxyhydroxides or discrete, crystalline Mn oxyhydroxides. This is suggested by the relatively lower sediment pH values and exchangeable contaminant metal in Zone II. Rose *et al.* (1979) propose that high exchangeable metal proportions indicate that a large proportion of the metal has formed by the relatively recent precipitation of soluble ions or flocculation of colloids from ground or surface waters. Relatively high proportions of exchangeable Pb, Zn, Cd and Mn, and specifically adsorbed Mn in Zone II suggest that recent contaminant metal-bearing Mn oxyhydroxide precipitation has occurred, possibly incorporating some of the released elements of Zone I. Increases in the proportion of easily reducible Fe (Figure 2) imply that some of the Fe oxyhydroxides may also have formed relatively recently.

Other evidence suggests that Fe and Mn oxyhydroxides have been accumulating within Zone II for a considerable period of time. Peaks in total Fe and Mn at 67–73 cm, 85–95 cm and 105–111 cm in Zone II (Figure 2) occur in sedimentary layers with rusty streaks and concretions. These peaks can be attributed to accumulations of zoned Fe (Figure 4c, d) and Mn oxyhydroxides. Corresponding peaks in total Zn, Cd and Cu, and easily and moderately reducible Pb, Zn, Cd and Mn suggest that these metals are associated with the oxyhydroxides. These easily and moderately reducible phases are probably more stable, and thus less soluble, than their exchangeable and specifically adsorbed counterparts described above.

The evidence for the breakdown and subsequent reprecipitation of Pb-, Zn-, Cd- and Cu-bearing Fe and Mn oxyhydroxides can be explained by fluctuating water-table conditions (cf. Gerrard, 1992). During a rise in water-table levels, Fe and Mn oxyhydroxides would break down by the reduction of Fe (III) and Mn (III, IV) to Fe (II) and Mn (II), releasing Pb, Zn, Cd and Cu. Mn (III, IV) compounds are more soluble than Fe(III) compounds (Garrels and Christ, 1965; Stumm and Morgan, 1970). When the water table falls, some of these mobilized species are oxidized and reprecipitated as amorphous Fe and Mn oxyhydroxides which could adsorb or co-precipitate the contaminant metals.

Zone III is characterized by moderate to high contents of specifically adsorbed Zn and Pb, and easily reducible Cd and Fe. These associations are not observed in contemporary overbank sediments (Macklin and Dowsett, 1989; Hudson-Edwards *et al.*, in press), suggesting that they are not depositional. They may instead be attributed to the further breakdown of contaminant metal-bearing oxyhydroxides under the suboxic to reducing conditions in Zone III, and a shift of metal associations towards more soluble and reactive fractions. This is corroborated by decreases in exchangeable Pb, Zn, Cd and Mn, moderately reducible Pb and Zn, and total Zn. High levels of oxidizable Pb, Cd, Cu and Fe may be due to the presence of reduced species of these metals in the sediments.

At Prudhoe, relatively high levels of exchangeable Pb, Zn, Cd and Mn, and oxidizable Zn, Cd, Cu, Fe and Mn occur in the upper part of the profile (Figure 3). These correspond to high loss on ignition percentages and abundant root material and wood charcoal. Relatively high contents of exchangeable contaminant metal are generally rare in contemporary overbank sediments (Macklin and Dowsett, 1989; Hudson-Edwards *et al.*, in press). The exchangeable metal could instead be related to the relatively low pH values (5.92 to 6.19) in this part of the profile. This could have been caused by the breakdown of the observed organic matter (cf. Rose *et al.*, 1979). Secondary redistribution of metals is also corroborated by the presence of Mn-Pb-Zn oxyhydroxides within charcoal fragments (Figure 4f).

Peaks in all of the total metal contents at 45–76 cm in the upper part of the profile coincide with peaks in specifically adsorbed Pb, Cd and Cu, easily and moderately reducible Pb and Zn, and decreases in oxidizable Pb, Zn, Cd, Cu and Mn. These features may be primary, depositional changes, or they could suggest that those contaminant metals leached from the upper part of the profile may have accumulated in Mn oxyhydroxides at the 45–76 cm level. Similar peaks in the lower part of the profile, over the interval 144–176 cm, may also have resulted from downward leaching and accumulation when the profile was at a lower height than at present. Root material (Figure 3) and zoned Fe oxyhydroxides at several levels between 45 and 182 cm support this assumption.

Low but detectable levels of exchangeable Pb, Zn and Cd throughout the Prudhoe profile suggest that the remobilization of these metals may be continuous. Significant amounts of oxidizable contaminant metal imply that the metals may be bound and possibly transported as organic complexes. Although most of the Cd appears to be in the oxidizable fraction, this may be an artifact of low amounts of Cd in the other fractions which are not detectable by AAS.

Implications of chemical remobilization for dating overbank alluvium using metal concentrations and ratios

Most of the Tyne basin chemostratigraphic dating has been carried out using total Pb and Zn concentrations and/or ratios with the assumption that these represent primary signatures (Macklin, 1986; Macklin *et al.*, 1992b). The evidence presented in this paper, however, suggests that chemical remobilization of Pb and Zn occurs in the profiles. While this has obvious implications for dating using total Pb and Zn concentrations, it may have little effect on Pb/Zn ratios if these metals are mobilized in similar amounts. The Blagill and Prudhoe data suggest that this is not the case:

- (1) The proportion of exchangeable Zn in both profiles is almost always greater than that of exchangeable Pb (Figures 2, 3).
- (2) Zn shows more drastic shifts towards more soluble fractions under assumed changing chemical conditions than Pb. The proportions of total and moderately reducible Zn decline sharply from Blagill Zone II to Zone III, while specifically adsorbed Zn increases. Analogous trends are not seen in the Pb patterns.
- (3) Zn-rich minerals appear to alter more readily than Pb-rich minerals. At Blagill, sphalerite alters to smithsonite, and both disappear down-profile, while cerussite persists. This may be a depositional change as discussed above, but may also be due to the lower solubility of cerussite relative to smithsonite (cf. Krauskopf, 1967).

All these factors suggest that Zn is more mobile than Pb in the Blagill and Prudhoe profiles. This has been observed in other field studies (e.g. Lewin *et al.*, 1977), and in experimental data. Many Fe, Al and Mn oxides show a greater affinity for Pb than Zn (Gadde and Laitinen, 1974; Murray, 1975; Forbes *et al.*, 1976; Kinniburgh *et al.*, 1976; McKenzie, 1980). In natural systems, Pb has a low solubility (Faust and Aly, 1981) and occurs principally in association with particulates or organic matter (Förstner and Patchineelam, 1976; Martin and Meybeck, 1979). Zn, in contrast, has a comparatively high solubility (Hem, 1972) and tends to exist principally in a dissolved form (Förstner and Wittmann, 1979).

Further evidence for modification of Pb/Zn ratios lies in the mineralogical and geochemical data. At Blagill, sphalerite and smithsonite may have been originally present in the lower part of Zone I, and in Zones II and III, but may have subsequently decomposed and/or been pseudomorphed. If this is the case, then the present Blagill Pb/Zn ratios will be considerably greater than their primary counterparts and the primary level of the 1880 changeover from Pb to Zn mining in the Pennines would presently be lower than the level calculated using these ratios. In addition, the largest change in Pb/Zn ratios occurs at the bottom of the profile. This level, however, cannot represent the year 1880 (when large-scale Zn mining began) because it lies below the stone wall dated to between 1840 and 1861.

Primary Pb/Zn ratios may also have been modified at Prudhoe. The Prudhoe profile in this study was sampled at the same location as that by Macklin *et al.* (1992b). These authors proposed that relatively rapid sedimentation and lack of bioturbation suggested that the post-depositional movement of Pb and Zn was insignificant. They suggested that the major part of the sequence was deposited in a 60 year period between

1890 and 1950. The Macklin *et al.* (1992b) data and the Prudhoe data obtained during this study differ significantly in terms of absolute concentrations and down-profile trends. If primary depositional concentrations of Pb and Zn had been preserved, as suggested by Macklin *et al.* (1992b), then the patterns should be virtually indistinguishable. High concentrations of Zn midway down the Macklin *et al.* (1992b) profile data may have resulted from post-depositional accumulation of downward-moving Zn complexes within Fe or Mn oxyhydroxides, or precipitation of Zn from groundwater, rather than primary Zn accumulation.

It is, however, very difficult to correct for post-depositional modifications to contaminant metal ratios because many of the essential variables cannot be well constrained. Factors such as (1) the exact amount of Pb and Zn deposited, (2) the original Pb- and Zn-bearing mineralogy, (3) the precise levels of the water table over time, (4) the amount of metal lost to biological activity, (5) the amount of soluble metal lost in ground or river water, (6) the amount of metal which has moved upwards or laterally, (7) the permeability of the sediment, and (8) the geomorphological history of the site, must be known before accurate calibrations can be made. Despite these limitations, very general estimates of the amount and distance of contaminant metal movement at Blagill and Prudhoe can be inferred. Zones of Fe oxyhydroxide accumulation occur over the intervals 67–73 cm, 85–95 cm and 105–111 cm in the Blagill profile, and 45–76 cm in the Prudhoe profile. This suggests that, in the extreme case, the contaminant metals could have moved as much as 111 cm at Blagill and 76 cm at Prudhoe. Even if the movements are only on the scale of centimetres, these are highly significant for precise, fine stratigraphic dating of sedimentary units where these are on the order of a few to tens of centimetres thick.

Significant decreases in total Zn, Cd and Cu in the upper part of Zone 1 at Blagill (Figure 2) may be depositional, but might also be explained by the breakdown of sphalerite and smithsonite. If true, these decreases correspond to potential losses of up to 90, 92 and 91 per cent of the Zn, Cd and Cu, respectively, from the sediment, assuming that sphalerite or smithsonite was originally present in the lower part of Zone I, and in Zones II and III. Similar decreases in total Zn, Cd and Cu contents from Zone II to III correspond to potential losses of up to 79, 91 and 49 per cent of the remaining Zn, Cd and Cu, respectively, from Zone II. These values are significantly higher than the maximum exchangeable Zn, Cd and Cu percentages (26, 50, 0, respectively; Figure 2). It is more difficult to estimate potential losses of Pb, given the persistence of cerussite throughout the profile, but exchangeable Pb percentages of up to 18 per cent within Zone II suggest that they may be considerable. Exchangeable Pb and Zn proportions of up to 4 and 19 per cent of the total Pb and Zn, respectively, suggest that metal fluxes within the Prudhoe profile may also be significant.

The evidence presented above for the secondary remobilization of contaminant metals in fine-grained alluvium that has experienced, or is presently experiencing, major changes in water-table levels, implies that Pb and Zn concentrations and ratios cannot be used for dating to the accuracy that was previously assumed. The extent to which remobilization of metals has occurred in floodplain deposits in other river systems affected by base-metal mining is presently unknown but post-mining bed degradation has been documented elsewhere in the UK (Lewin *et al.*, 1983; Taylor and Lewin, 1996), continental Europe (Leenaers, 1989; Macklin and Klimek, 1992) and North America (Graf, 1994). This appears to apply to many sites in the Tyne basin where, as a consequence of channel incision since the end of the nineteenth century, near-river water-table levels have progressively fallen. It is also not clear whether humid river systems that experienced relatively frequent but small fluctuations in valley-floor groundwater levels are more susceptible to metal remobilization than rivers in dryland environments where changes are periodic but more extreme. Research is required in semi-arid and arid environments to evaluate this.

Although the bulk of the evidence presented here argues against using only Pb/Zn ratios for dating, caution should also be employed when using other metals. Mn and Fe oxyhydroxides are known to adsorb or co-precipitate metals such as Co, Ni, and As (e.g. Taylor and McKenzie, 1966; Laxen, 1983) and these may be remobilized during changes in pH and redox. Total contaminant metal concentrations have been used in many fluvial, lacustrine and marine environmental analyses to distinguish contaminated from uncontaminated sediment (e.g. Allan, 1974; Schaule and Patterson, 1981; Rippey *et al.*, 1982; Macklin *et al.*, 1985). Workers in these areas should appreciate that uncontaminated sediment may become contaminated through secondary metal movement and reprecipitation or adsorption of metals onto 'clean' sediment. Similarly, the degree of original contamination may be under-estimated due to secondary leaching processes, unless the contaminant metal-bearing minerals are insoluble in their respective environments.

CONCLUSIONS

- (1) Pb, Zn, Cd and Cu are presently stored in Tyne basin overbank sediments at Blagill and Prudhoe as sulphides, carbonates, and Fe and Mn oxyhydroxides. At Blagill, a down-profile weathering paragenesis, whereby sulphides alter to carbonates and both alter to, and are supplanted by, Fe and Mn oxyhydroxides, is observed.
- (2) The distribution of Pb, Zn, Cd and Cu can be explained by a combination of primary (depositional) and secondary (remobilizational) factors. Evidence for chemical remobilization includes: mineral breakdown and pseudomorphing, high levels of exchangeable and specifically adsorbed contaminant metal in zones of relatively low pH, and the accumulation of secondary Fe and Mn oxyhydroxides at levels related to a fluctuating water table or the breakdown of organic matter.
- (3) The distance that the contaminant metals could have been translocated down-profile is interpreted to range from a few centimetres up to about 45–111 cm. This implies that, in degrading river systems that have experienced, or are experiencing, major changes in water-table levels or breakdown of organic matter, fine-unit (centimetre-scale) stratigraphy using metal concentrations and ratios should not be attempted. Coarse-scale (0.5 m to metre-scale) chemostratigraphy will still provide a means of separating pre-, peak- or post-industrial units, but every attempt should be made to discern the level of remobilization that has occurred.

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